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14. ABSTRACT The first standard molar enthalpy of combustion and resultant heat of formation were determined for a binary heterocyclium <i>closo</i> -icosahedral dodecaborane [B ₁₂ H ₁₂] salt selected from a number of recently synthesized water and air-stable salt analogues that represent a new family of high energy materials. Two heterocyclic 1-amino-3-H-1,2,3-triazolium cations, stoichiometrically paired with the unique [<i>closo</i> -B ₁₂ H ₁₂] ²⁻ di-anion, formed a 99.2% pure [1AT3H] ₂ [<i>closo</i> -B ₁₂ H ₁₂] salt that revealed a standard enthalpy of combustion ($\Delta_c H^\circ$) equal to $-(12675.9 \pm 3.5)$ kJ/mol or $-(3029.6 \pm 0.8)$ kcal/mol. Using the Hess thermochemical cycle, the standard molar heat of formation was determined to be $\Delta_f H^\circ$ (solid) = $-(25.1 \pm 3.5)$ kJ/mol or $-(6.0 \pm 0.8)$ kcal/mol. These thermochemical values are significantly higher than those reported for the only other type of <i>closo</i> -borane based salts that paired two acyclium (ammonium, hydrazinium, or guanidinium) cations with the lower [<i>closo</i> -B ₁₀ H ₁₀] ²⁻ di-anion homologue. These [acyclium] ₂ [<i>closo</i> -B ₁₀ H ₁₀] salts required an accelerant compound to promote complete combustion, but the heterocyclic-based [1AT3H] ₂ [<i>closo</i> -B ₁₂ H ₁₂] salt provided the best combustion values as a single entity.					
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First heat of formation determined from experimental standard molar enthalpy of combustion values for a high energy binary heterocyclium *closo*-icosahedral dodecaborane salt: [1-Amino-3-H-1,2,3-triazolium]₂[*closo*-B₁₂H₁₂] (Preprint)

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Abstract

The first standard molar enthalpy of combustion and resultant heat of formation were determined for a binary heterocyclium *closo*-icosahedral dodecaborane [B₁₂H₁₂] salt selected from a number of recently synthesized water and air-stable salt analogues that represent a new family of high energy materials. Two heterocyclic 1-amino-3-H-1,2,3-triazolium cations, stoichiometrically paired with the unique [*closo*-B₁₂H₁₂]²⁻ di-anion, formed a 99.2% pure [1AT3H]₂[*closo*-B₁₂H₁₂] salt that revealed a standard enthalpy of combustion ($\Delta_c H^\circ$) equal to $-(12675.9 \pm 3.5)$ kJ/mol or $-(3029.6 \pm 0.8)$ kcal/mol. Using the Hess thermochemical cycle, the standard molar heat of formation was determined to be $\Delta_f H^\circ(\text{solid}) = -(25.1 \pm 3.5)$ kJ/mol or $-(6.0 \pm 0.8)$ kcal/mol. These thermochemical values are significantly higher than those reported for the only other type of *closo*-borane based salts that paired two acyclium (ammonium, hydrazinium, or guanidinium) cations with the lower [*closo*-B₁₀H₁₀]²⁻ di-anion homologue. These [acyclium]₂[*closo*-B₁₀H₁₀] salts required an accelerant compound to promote complete combustion, but the heterocyclic-based [1AT3H]₂[*closo*-B₁₂H₁₂] salt provided the best combustion values as a single entity.

Keywords: Standard molar enthalpy of combustion, Heat of formation, Isoperibol bomb calorimetry, Heterocyclium *closo*-dodecaborane salts, *Closo*-borane di-anion salts

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1. Introduction

The first published standard molar enthalpy of combustion and associated heat of formation for a new type of recently synthesized binary heterocyclium icosahedral *closo*-borane salt were experimentally determined. The [1-amino-3-H-1,2,3-triazolium]₂[*closo*-B₁₂H₁₂], or [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1**), is one of a number of newly reported analogous heterocyclium borane-based salts that comprise a new family of high energy materials [1-3]. The standard molar enthalpy of formation for [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1**), based upon an observed experimental heat of combustion results, was obtained using a reliable isoperibol bomb calorimetry method. This high energy solid [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1**) could be thermally initiated to a rapid self-sustained combustion in air, as could two other related icosahedral binary [4-amino-1-H-1,2,4-triazolium]₂[*closo*-B₁₂H₁₂] and [5-aminotetrazolium]₂[*closo*-B₁₂H₁₂] salts, (**2**) and (**3**), respectively [2]. Salt (**1**) also gave minimum 100% non-initiation thresholds of 84 Kg-cm for impact [3] and 16.8 Kg-cm for friction, but initiated at 0.16 Joules which was the lowest charge used in our ESD tests.

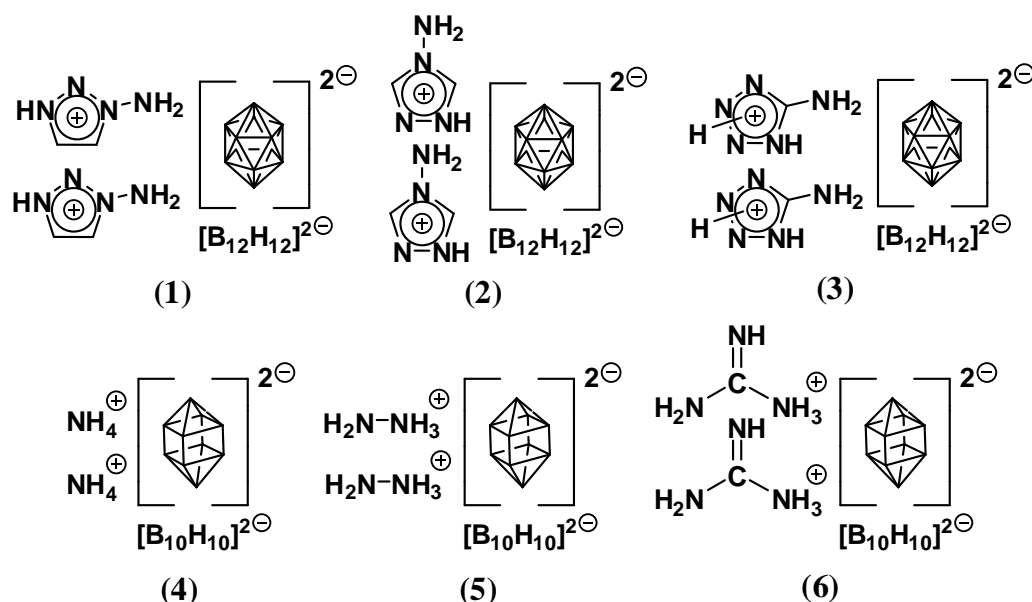


Fig. 1. Three binary [heterocyclium]₂[*closo*-B₁₂H₁₂] salts (**1-3**) containing the *closo*-[B₁₂H₁₂]²⁻ di-anion compared to three binary [acyclinium]₂[*closo*-B₁₀H₁₀] salts (**4-6**) containing the lower *closo*-[B₁₀H₁₀]²⁻ homologue.

Binary [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1**), as well as salts (**2**) and (**3**), contain the unique icosahedral-sized, three dimensional polyhedral-shaped [*closo*-B₁₂H₁₂]²⁻ di-cation (Fig. 1), which was first prepared as the triethylammonium salt in 1960 [4], and which forms salts of low toxicity and high thermal stability [5]. This novel [*closo*-B₁₂H₁₂]²⁻ di-anion has been asserted to be the most stable covalently bonded chemical entity in all of chemistry [6], and with 26 delocalized valence electrons in its negatively two-charged σ -bonded framework, represents a “super-aromatic” polyhedral-shaped counterpart of the planar benzene molecule [6,7]. Salt (**1**) belongs to a new type of icosahedral [*closo*-B₁₂H₁₂]²⁻ borane [1-3,8], [*closo*-CB₁₂H₁₂]²⁻ carborane [1-2,8-12], and [*closo*-B₁₂F₁₂]²⁻ perfluoroborane [8] salts where two planar aromatic heterocyclium mono-cations, each

with six delocalized π -electrons, are stoichiometrically paired with the 3-dimensional polyhedral aromatic borane-based anionic species which contain multiple delocalized σ -electrons [1].

The standard molar enthalpy of combustion and resultant heat of formation only have been reported twice for salts (**4-6**) that contain a polyhedral-type *closo*-borane structure [12,13] seen in the lower portion of Figure 1. These salts (**4-6**) each contained the sigma-delocalized lower [*closo*-B₁₀H₁₀]²⁻ di-anion homologue which was paired with two singly positively-charged ammonium cations (**4**) [12,13], hydrazinium cations (**5**) [12], or guanidinium cations (**6**) [12].

Standard molar enthalpy of combustion and resultant heat of formation values for [1AT3H]₂[*closo*-B₁₂H₁₂] **1** are the first to be reported for a salt that contains an icosahedral [*closo*-B₁₂H₁₂]²⁻ di-anion as well as the first salt which contains a [*closo*-B₁₂H₁₂]²⁻ di-anion that is paired with two heterocyclium cations. An experimentally determined standard molar enthalpy of combustion equal to $-(12675.8 \pm 3.5)$ kJ/mol, or $-(3029.4 \pm 0.8)$ kcal/mol, was obtained by averaging the three experimental runs taken on a 99.2% pure [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1b**) sample. Using the Hess thermochemical cycle, a $-(25.2)$ kJ/mol, $-(6.0 \pm 0.8)$ kcal/mol, or $-(0.019)$ kcal/g standard molar heat of formation is calculated for this binary 99.2% pure heterocyclium salt (**1b**). This resultant standard molar enthalpy heat of formation value for the [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1b**) is significantly higher than these same thermochemical values that previously were reported for the binary acyclinum salts (**4-6**) which contain the smaller [*closo*-B₁₀H₁₀]²⁻ di-anion homologue [12,13] paired stoichiometrically with two non-cyclic ammonium, hydrazinium, or guanidinium singly-charged cations.

2. Experimental

The experimental heat of combustion determinations were performed with two different sample purities (94.8% and 99.2%) of the [1-amino-3-H-1,2,3-triazolium]₂[*closo*-B₁₂H₁₂] salt (**1**). Experimental runs with the [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1**) were conducted on an approximately half-gram scale, both singularly and in the presence of the benzotrifuroxan (BTF) explosive (**7**), which was purported to be a necessary combustion accelerant for salts (**4-6**) that were tested on a milligram scale [12]. The BTF (**7**) sample was graciously provided by the Naval Air Warfare Center (NAWC), China Lake, CA.

2.1. Equipment

Experimental heat of combustion runs for the [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1**) were conducted using a Parr 1266 Isoperibol Oxygen Bomb Calorimeter in conjunction with two different oxygen combustion bombs. An 1108 Oxygen bomb was used for sample runs conducted with only the [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1**). For the pure BTF explosive (**7**), a heavy-walled Parr 1104 combustion bomb (240 mL capacity) was used and for combustion determinations when both the BTF (**7**) compound and the subject [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1**) were combusted together as separately stacked pellets designated as [1AT3H]₂[*closo*-B₁₂H₁₂]/BTF. The Parr 1104 combustion bomb was designed to handle explosives and other fast burning high energy samples capable of liberating up to 12,000 calories using an oxygen charging pressure up to 45 atm (655 psig). The combustion runs were modeled after ASTM D 240-87, "Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter." All heat of

combustion results were an average value for at least three separate determinations bracketed by benzoic acid (**8**) pellet standard quality control checks.

Standardization of the 1266 Isoperibol calorimeter and 1108 combustion bomb was performed by combusting about 1 gram benzoic acid pellets from Parr, Lot Code 081007 to achieve an energy equivalent value of ϵ (calorimeter, 1108) = (2410.4699 ± 0.7563) cal/°C based on ten runs. Standardization of the 1266 Isoperibol calorimeter and 1104 combustion bomb was performed by combusting about 1.4 gram benzoic acid pellets, Parr, Code 081007 to achieve an energy equivalent value of ϵ (calorimeter, 1104) = (2505.0526 ± 0.5786) cal/°C based on five runs. The uncertainty associated with this energy equivalent represented the standard deviation of the mean, and the quantity ± 0.5786 cal/°C implied a precision of 0.05% for the standardization for the 1266 Parr Isoperibol calorimeter and 1104 oxygen combustion bomb.

Boron and potassium sample content were determined in diluted aqueous experimental samples using an Agilent 7500ce Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Santa Clara, CA, equipped with peltier cooled Scott-type double-pass spray chamber set at 10 °C and self-aspirating MicroFlow PFA-100 nebulizer (ESI, Omaha, NE) operated with a carrier gas flow rate of 1 L/min. A flow rate of 4 mL/min. was used in the collision cell to minimize potential spectroscopic interferences. The isotopes monitored for percent quantitation were ^{11}B and ^{39}K .

The percent of residual chloride ion content in the re-crystallized $[\text{1AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt **1b** sample was determined by Ion Chromatography (IC) using a Waters 1525 HPLC Binary Pump equipped with a Waters 432 conductivity detector and a

Phenomenex™ STAR-ION™ A300 100 x 4.6 mm ID (PEEK™) column. A 0.0301 mg sample of salt (**1b**) was weighed into a plastic class B centrifuge tube and diluted to 25 mL using Type 1 ultra-pure water. The aqueous sample was heated to 80 °C with a plastic reflux cap to ensure complete dissolution. Upon cooling to room temperature, the sample was passed through an IC Millex LG 0.2um syringe filter prior to injection. A three point calibration curve was generated using blank reagent water, 1 and 10 ppm NIST traceable chloride standard. The chloride ion concentration content was determined by comparing peak area response of the samples to the standard calibration curve.

2.2. Synthesis of 1-amino-3-H-1,2,3-triazolium *closo*-dodecaborane salt (**1**) or $[1AT3H]_2[*closo*-B_{12}H_{12}]$

The previously described synthesis [1] of the $[1AT3H]_2[*closo*-B_{12}H_{12}]$ salt (**1**) required a larger-scale effort. This was accomplished by the direct scale-up of two different batch syntheses using an appropriate stoichiometry of the 1-amino-3-H-1,2,3-triazolium chloride, $C_2H_5N_4Cl$, and potassium *closo*-dodecaborane, $K_2[*closo*-B_{12}H_{12}]$, salt reactants. The 1-amino-3-H-1,2,3-triazolium chloride reactant salt was synthesized [1] from 1-amino-1,2,3-triazole, using a literature method [13]. The $K_2[*closo*-B_{12}H_{12}]$ reactant salt was purchased from Katchem Ltd., E. Krasnohorske 6, 110 00 Prague 1, Czech Republic and was used as received.

2.2.1. First Batch of $[1AT3H]_2[*closo*-B_{12}H_{12}]$ Crude Salt (**1**)

A deep-red solution consisting of [1AT3H]Cl (4.822 g; 40.00 mmol) and $K_2[closo-B_{12}H_{12}]$ (4.400 g; 20.00 mmol) dissolved in 8 mL of de-ionized (DI) water were heated to reflux and then was cooled in the refrigerator to 3.5 °C over five days whereupon massive crystals formed. The solid was filtered and rinsed with 1.5 mL pre-chilled (3.5 °C) DI water. The resulting solid was then dried at room temperature under high vacuum (96 hr at 100 mTorr to afford 4.700 g of smallish, reddish-tinged crystals (crude yield = 75.3 %).

2.2.2. Second Batch of Crude [1AT3H]₂[closo-B₁₂H₁₂] Salt (**1**)

The synthesis was accomplished in the same manner as Batch 1. In this case, [1AT3H]Cl (6.027 g; 50.00 mmol) and $K_2[closo-B_{12}H_{12}]$ (5.508 g; 25.03 mmol) were dissolved in 11.5 mL DI water, and upon high vacuum drying (96 hr at 100 mTorr, afforded 7.654 g of crude product (yield = 98.2%).

2.2.3. Original [1AT3H]₂[closo-B₁₂H₁₂] Salt (**1a**)

Both the first and second batches of the crude [1AT3H]₂[B₁₂H₁₂] salt (**1**) were combined along with former smaller samples of salt (**1**) of nearly equivalent purity (total combined sample = 16.60 g). The combined sample was partially dissolved in AR methanol (*c.a.* 50 mL) at reflux temperature. The insolubles were removed by filtration, and the red-orange solution was treated with Darco™ (1.5 g). The resultant slurry was then filtered through a prepared bed of Celite™ (*c.a.* 2.5 g). The filtrate solution was reduced in volume at reflux until solid began to crystallize. Upon filtration, and drying, 14.86 g of solid were isolated. This solid was slurried in AR diethyl ether and re-filtered

to give, upon drying, 14.78 g of solid salt (**1a**) product. This salt (**1a**) sample was determined by ICP-MS ^{11}B [15] and ^{39}K analysis (2.6% impurity) to be 94.8% pure. Because of the double metathesis synthesis method used, it was assumed the remaining 2.6% impurity would be the chloride ion which verified a 94.8% purity for this original salt (**1a**) by weight. This assumption also was supported by ICP-MS and IC analyses that showed the presence of residual KCl by-product in the re-crystallized salt (**1b**) sample described below. The 94.8% pure salt (**1a**) was used in the initial heat of combustion determination.

2.2.4. Re-crystallized $[\text{LAT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ Salt (**1b**)

From 14.86 g of 94.8% pure salt (**1a**) sample, 6.00 g were taken for further purification. The 6.00 g subset was re-crystallized from 8 mL of DI water where the dissolved sample was brought to reflux and cooled in the refrigerator (3.5 °C) for three days to form solid crystals. The solid was recovered by filtration and the resultant solid was rinsed with 1 mL of pre-chilled (3.5 °C) DI water. The solid was dried at room temperature under high vacuum (100 mTorr) in a Electrothermal[®] ChemDry[®] thermal drying apparatus at 90 °C for three days to give 4.738 g of an off-white solid (Recovery = 79.0%). This salt (**1b**) sample gave satisfactory a 400 Hz ^1H NMR (DMSO- d_6 , center peak = 250 Hz), a 100 Hz ^{13}C NMR (DMSO- d_6 , center peak = 39.51 Hz) values as well as an FTIR (HATR method) spectrum that agreed with published values [1]. While ICP-MS analysis for boron showed a 100.4% recovery, the experimental precision variance for this analysis was demonstrated to be from 99.0% to 102.4% with a certified standard boron

sample [15]. However, ICP-MS analysis of this sample revealed 0.4 % potassium, and ion chromatography found 0.4% chloride (KCl by-product = 0.8% by weight) giving a 99.2% pure sample of re-crystallized salt (**1b**). Therefore, this re-crystallized [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1b**) used in the final heat of combustion runs was adjudged to be 99.2% pure.

2.2.5. Heat of Combustion Sample Preparation and Analyses

All samples of the subject [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1**) and the benzotrifuroxan (**7**) compound were pressed into disk-like pellets using a remotely-controlled press apparatus. Benzoic acid (**8**) pellets from Parr were tested before and after each [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1**) run as a quality control check to ensure that the calorimeter and the method employed provided consistent combustion results. In obtaining a heat of combustion for the BTF (**7**) compound, benzoic acid (**8**) was used to spike the BTF sample (**7**) in each run for ensuring

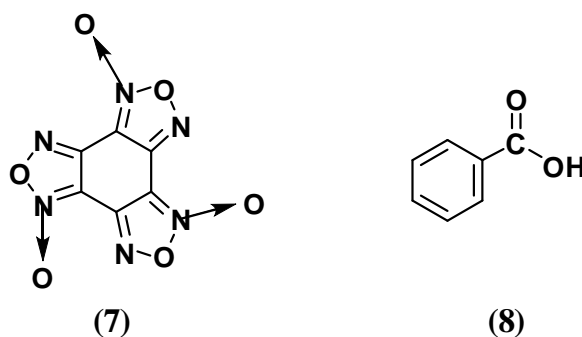


Fig. 2. Chemical structures of benzotrifuroxan (**7**) [BTF] and benzoic acid (**8**) [BA].

complete combustion before calculating its respective experimental heat of combustion.

The combustion of the recrystallized [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1**) in the presence of

BTF (7) was also conducted in the Parr 1104 Oxygen bomb. One combustion run resulted in an incomplete combustion of the BTF (7) and benzoic acid (8) pellets when the BA (8) pellet was placed on top of the benzotrifuroxan pellet. Subsequent runs involved stacking the benzotrifuroxan pellet on top of the benzoic acid pellet and resulted in consistent and complete combustion of the BTF (7) sample. Table 1 and Table 2 in the Results and Discussion section cover the conversion of the observed experimental heat of combustion to the standard molar enthalpy of combustion for BTF (7) and BA (8).

In all combustion experimental runs, the nitric acid energy was subtracted from the overall observed energy, as is illustrated in Table 1 and Table 2 and accompanied by a textual discussion of each, revealed that the excellent experimentally determined standard enthalpy of combustion values of BTF (7) and benzoic acid (8) were achieved when compared to the published NIST values of both.

When a combined $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]/\text{BTF}$ sample was combusted in the 1104 combustion bomb in the presence of oxygen at 440 psi, the observed experimental heat of combustion results again varied with the stacking order of the two pellets. Because this Paar 1104 oxygen bomb was designed for combustion tests of explosives, all samples involving the BTF (7) explosive/ $[1\text{ATH}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt pellets were combusted in the Paar 1104 combustion bomb. Higher observed experimental heat of combustion results were obtained when the $[1\text{ATH}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (1) pellet also was placed atop the BTF (7) pellet; however, neither stacking method produced an observed experimental heat of combustion result as high as that exhibited by the single $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (1) pellet samples.

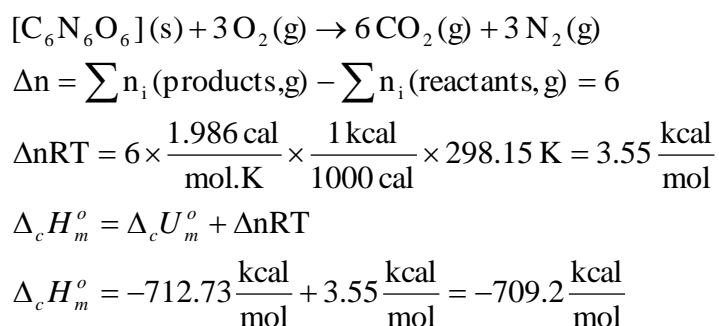
Upon opening the combustion bomb after each experiment, the bomb was washed with warm de-ionized water (18 mega-ohm purity level), and the correction for the energy of formation of aqueous nitric acid produced during the combustion process, was determined by the neutral titration with a standardized sodium hydroxide solution (0.4039 N) using a methyl red indicator to determine the titration end point. The heat of formation for the aqueous nitric acid in the oxygen bomb was derived from the equation from ASTM D240-87, Q_{HNO_3} in Joules = mL of standard (0.0866 N) NaOH solution used in titration x 5.

When determining the heat of combustion ($\Delta_c U^{\text{exp}}$) for BTF (7) (Table 2), where benzoic acid (8) was simultaneously present as a spike, the energy contributed by the mass of benzoic acid pellet (8) used in each combustion run was subtracted based on its declared heat of combustion value of – (6318) cal/g. Also the correction discussed for the heat of formation from the nitric acid formed from the combustion reaction was applied to each combustion run including the benzoic acid (BA) quality control runs, seen in Table 1, to ensure that the calorimeter was generating accurate and reproducible results. This also provided the BTF observed experimental heat of combustion ($\Delta_c U^{\text{exp}}$) values recorded in Table 2. Parr platinum wire was used to initiate combustion for all runs and did not contribute to the observed experimental heat of combustion ($\Delta_c U^{\text{exp}}$) value because its heat of fusion is zero calorie.

Depending on the compound or salt being considered, standard enthalpy of combustion ($\Delta_c H^\circ$) values in kJ/mol, and kcal/mol, were calculated from the experimental heat of combustion value ($\Delta_c U^{\text{exp}}$) in the cal/g unit. This derived calculation was performed by converting the observed experimental cal/g value ($\Delta_c U^{\text{exp}}$) to a molar heat of combustion

kcal/mol value using the respective compound or salt formula weight, correcting for the gas volume change (ΔnRT) as shown in Eq. (1, 2, 3, 4, or 5), converting Δn to standard conditions in kcal/mol units (ΔnRT), and subtracting or adding, respectively, the standard (ΔnRT) molar gas change from the constant volume combustion energy of the compound or salt being considered. Eq. (6) then displays the conversion of the standard enthalpy of combustion ($\Delta_c H^\circ$) into the final standard molar enthalpy of formation ($\Delta_f H^\circ$) which is illustrated for the subject 99.2% pure [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1b**). In all heat of formation calculations, the standard molar heat of formation ($\Delta_f H^\circ$) for known chemical compounds was obtained from the NIST Standard Reference Database 69 NIST Chemistry, *NIST Chemistry WebBook* [16].

Demonstrated in Eq. 1 is an example of the BTF (**7**) compound being converted from the experimentally determined heat of combustion result, after applying the BTF (**7**) compound molecular weight to obtain the molar heat of combustion [(-712.73) kcal/mol], for calculating the BTF standard molar enthalpy of combustion value of -(709.2) kcal/mol or -(2967.3) kJ.mol.



(1)

3. Results and Discussion

The first standard molar enthalpy of combustion and resultant heat of formation values were determined for 1-amino-3-H-1,2,3-triazolium *closo*-dodecaborane, or $[1AT3H]_2[closo-B_{12}H_{12}]$ salt (**1**), which contains an *closo*-icosahedral-sized $[B_{12}H_{12}]^{2-}$ di-anion. These important thermochemistry values also were the first obtained for any type of *closo*-borane di-anion that is paired stoichiometrically with two singly charged heterocyclium-type cations.

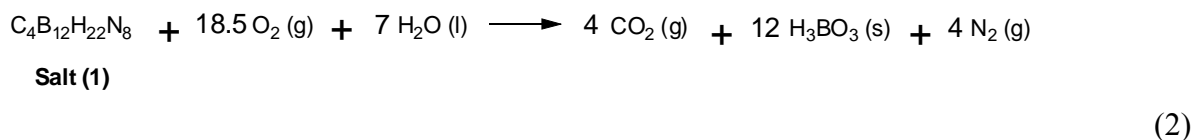
Previous experimental enthalpy of combustion and derived heat of formation results were conducted with salts (**4-6**) which contain the smaller polyhedral $[closo-B_{10}H_{10}]^{2-}$ di-anion that is stoichiometrically paired with two acyclic ammonium, hydrazinium, or guanidium cations [12], respectively. Conducted on a milligram scale with the salts (**4-6**), this previous investigation reported that it was necessary to use the explosive BTF (**7**) as a combustion accelerant to promote the complete combustion of $[acyclinum]_2[closo-B_{10}H_{10}]$ salts (**4-6**) [12] by oxidation of all the inorganic boron to boric acid. In another earlier enthalpy of combustion study of the $[NH_4]_2[closo-B_{10}H_{10}]$ salt (**4**), vinylidene fluoride polymer was used as a combustion promoter in a rotating-bomb calorimeter that contained an excess of aqueous HF solvent and formed an aqueous HBF_4 product [13]. For our experimental studies, this latter method was impractical; however, use of the BTF (**7**) as a potential combustion accelerant was an acceptable alternative for this new $[1AT3H]_2[closo-B_{12}H_{12}]$ salt (**1**) investigation.

The first set of experimental heat of combustion runs were conducted with the originally synthesized $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (**1a**), determined later to be 94.8% pure by weight, using no BTF (7) combustion accelerant. Five benzoic acid (**8**) quality control runs also were used as a benchmark for calorimeter performance. The respective heat of combustion results ($\Delta_c U^{\text{exp}}$) are shown for each run of salt (**1a**) and benzoic acid (**8**) in Table 1. An averaged experimental heat of combustion ($\Delta_c U^{\text{exp}}$) equal to – (9094.42) cal/g was obtained for the $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (**1a**) based on three combustion runs (Table 1). The five benzoic acid (**8**) experimental runs were conducted both before and after the original $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (**1a**) experiments to ensure that all values obtained from one experimental run to another were consistently accurate and reproducible.

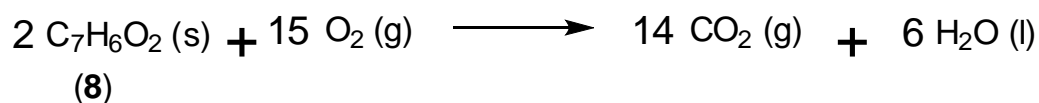
Table 1. Observed heat of combustion results for original $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (**1a**) and the benzoic acid (**8**) quality control standard

Run No.	Sample Used	Sample Mass (g)	Nitric Acid (cal)	Experimental $\Delta_c U^{\text{exp}}$ (cal/g)	$\Delta_c U^{\text{exp}}$, Three Run Averaged (cal/g)
Q. C. Standard	Benzoic Acid (BA)	0.9954	10.02	–6314.4591	-----
1	Salt (1a)	0.6490	13.26	–9088.0450	See Below
Q. C. Standard	Benzoic Acid (BA)	0.9933	10.16	–6321.8385	-----
Q. C. Standard	Benzoic Acid (BA)	0.9994	9.73	–6317.9498	-----
2	Salt (1a)	0.6583	20.32	–9098.0781	See Below
Q. C. Standard	Benzoic Acid (BA)	1.0065	10.58	–6318.5566	-----
3	Salt (1a)	0.6486	12.70	–9097.1232	–9094.42
Q. C. Standard	Benzoic Acid (BA)	1.0201	10.30	–6333.4384	-----

The averaged $- (9094.42)$ cal/g observed experimental heat of combustion ($\Delta_c U^{\text{exp}}$) for salt (**1a**) in Table 1 was conducted using the Parr 1108 combustion bomb. The standard enthalpy of combustion ($\Delta_c H^\circ$), based on this observed experimental $- (9094.42)$ cal/g heat of combustion ($\Delta_c U^{\text{exp}}$) for the salt (**1a**) with a MW = 312.00 g/mol, was converted to $- (2831.24)$ kcal/mol using calculations based on Eq. (2 and 5). Eq. (2) was the same chemical equation that was previously used for salts (**4-6**) [13]. The $- (2831.24)$ kcal/mol standard enthalpy of combustion value, using Eq. (6), provided a standard heat of formation ($\Delta_f H^\circ$) equal to $- (855.2)$ kJ/mol or $- (204.4)$ kcal/mol for this original 94.8% pure $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (**1a**) sample.



The five benzoic acid (**8**) observed heat of combustion ($\Delta_c U^{\text{exp}}$) values gave an average value of $- (6321.2)$ cal/g in Table 1. When this experimentally derived $- (6321.2)$ cal/g value was dimensionally transformed with the BA (**8**) molecular weight (MW = 122.12 g/mol), brought to standard conditions by correcting for the reduction of one mole of gas during the benzoic acid combustion (Δn) as illustrated in Equation (3), substitution into Equation (5) provided an experimentally derived standard enthalpy of combustion

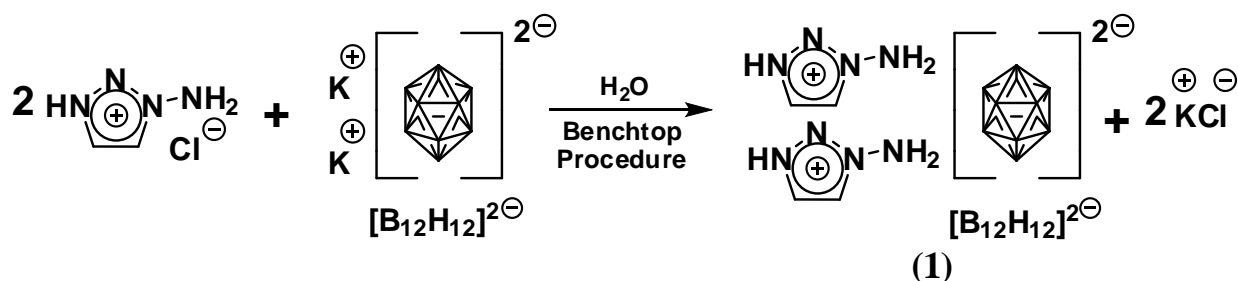


(3)

($\Delta_c H^\circ$) value equal to $-(3227)$ kJ/mol or $-(771.3)$ kcal/mol. This value for the benzoic acid (**8**) quality control standard also was in excellent agreement with the published NIST Standard Reference Database 69 NIST Chemistry, *NIST Chemistry WebBook* condensed phase $\Delta_c H^\circ$ value of $-(3228 \pm 4)$ J/mol or $-(772 \pm 1)$ kcal/mol [16]. This value was back calculated to demonstrate the hypothetical $-(6325 \text{ to } 6309)$ cal/g experimental heat of combustion ($\Delta_c U^{\text{exp}}$) range for benzoic acid (**8**). Thus, the average $-(6321.2)$ cal/g heat of combustion ($\Delta_c U^{\text{exp}}$) value for BA (**8**) in Table 1 was very close to the accepted published result of $-(6318)$ cal/g and reflected proper calorimeter standardization and performance.

Because of the lower than anticipated standard heat of formation ($\Delta_f H^\circ$) result for salt (**1a**), the analytical purity of this original $[1\text{AT3H}]_2[\textit{closo}\text{-B}_{12}\text{H}_{12}]$ salt (**1a**) sample was determined to ensure that the heat of combustion ($\Delta_c U^{\text{exp}}$) and derived heat of formation results obtained from the Table 1 values were meaningful and representative of the salt (**1a**) purity. Elemental boron and potassium analyses using an ICP-MS instrument were performed on aqueous diluted samples of the original salt (**1a**) sample to determine the percentage of each element present. After calibrating the ICP/MS with certified boron and potassium standards with dilution factors appropriate for this analysis, the original $[1\text{AT3H}]_2[\textit{closo}\text{-B}_{12}\text{H}_{12}]$ salt (**1a**) sample displayed only 94.8% of the expected boron content. Boron quality control checks were very consistent and reproducible at the 20-200 ng/mL levels yielding analytical recovery results ranging from 99.0 to 102.4%. The ICP/MS determined 94.8% boron purity in the original salt sample (**1a**) is further supported by the 2.6% level of the potassium cation also found to be present in salt (**1a**). Assuming the remaining 2.6% of salt (**1a**) was the chloride anion paired with the

potassium cation, the original [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1a**) was only 94.8% pure by weight and contained an accompanying 5.2% potassium chloride salt impurity. Given the synthesis procedure used for the [1AT3H]₂[*closo*-borane] salt (**1**) [1], KCl was the most likely contaminant (Scheme 1). Subsequent purity analyses on a water re-crystallized sample of original salt (**1a**), to provide a later re-crystallized 99.2% pure [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1b**) sample, also strongly supported this suspicion.



Scheme 1. Synthesis of [1-amino-3-H-1,2,3-triazolium]₂[*closo*-dodecaborane] salt (**1**).

The 94.8% pure [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1a**) experimental heat of combustion ($\Delta_c U^{\text{exp}}$) of -(9096.42) cal/g and a standard molar enthalpy of combustion ($\Delta_c H^\circ$) of -(2843.59) kcal/mol, substituted into Eq. (2, 4, and 5) yielded a standard molar heat of formation ($\Delta_f H^\circ$) equal to -(855.2) kJ/mol or -(204.4) kcal/mol. Quite reasonably, these corresponding thermochemical values for a purer salt (**1**) certainly would increase in value. If a correlation exists between compound purity and its respective heat of combustion based on a linear fit model, the -(9096.42) cal/g experimental heat of combustion for the 94.8% pure salt (**1a**) then would theoretically yield an experimental heat of combustion of -(9593.27) cal/g for a 100% pure salt (**1**). This extrapolated value would produce a

respective standard enthalpy of combustion via Eq. (2 and 5) equal to $-(2999.32)$ kcal/mol and a derived standard molar heat of formation using Eq. (6) would increase to $-(152.0)$ kJ/mol or $-(36.3)$ kcal/mol.

An attempt to purify the 94.8% salt **1a** sample more closely to a 100% purity by aqueous re-crystallization was conducted and yielded a significantly purer $[1\text{AT3H}]_2[\textit{closo}\text{-B}_{12}\text{H}_{12}]$ salt (**1b**), albeit with a considerable amount of salt product loss. Purified salt (**1b**) analyses for boron and potassium content via ICP-MS analyses, and for chloride content using ion chromatographic (IC) analysis revealed a 99.2% purity. Although the ICP-MS showed a 100.4% boron percentage in the salt [15], ICP-MS also detected a 0.4% potassium impurity. Additionally, an ion chromatography chloride analysis complemented the ICP-MS potassium cation analysis by revealing 0.38% (0.4%) of the paired chloride anion to be present in this re-crystallized salt (**1b**) sample. Based on the presence of 0.8% KCl impurity by weight, the re-crystallized $[1\text{AT3H}]_2[\textit{closo}\text{-B}_{12}\text{H}_{12}]$ salt (**1b**) was adjudged to be 99.2% pure.

This limited quantity of the re-crystallized $[1\text{AT3H}]_2[\textit{closo}\text{-B}_{12}\text{H}_{12}]$ salt (**1b**) was then used to determine whether or not a BTF (**7**) accelerant was necessary to effect complete combustion of salt (**1b**) in this thermochemical investigation like that needed in the earlier investigation of the acyclinum *closo*-decaborane salts **4-6** [12]. First, however, the heat of combustion for the BTF (**7**) sample needed to be experimentally measured and compared with the published NIST value for this high energy compound to validate our experimental method using the Parr 1104 combustion bomb. The BTF (**7**) experimental runs were

conducted in the presence of benzoic acid (**8**) whose purity was declared to be of standardization quality.

In determining the heat of combustion for BTF (**7**), a benzoic acid (**8**) pellet was stacked with the BTF (**7**) pellet in the combustion cup. The first combustion determination with BTF (**7**) involved incomplete combustion (run 2) in which the benzoic acid pellet was placed atop the BTF (**7**) pellet. A similar behavior resulted with the $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (**1b**)/BTF run 6 when the BTF (**7**) pellet was placed atop the salt (**1b**) pellet. Best results were achieved when the BTF (**7**) pellet was placed atop a benzoic acid (**8**) pellet (runs 3-5), and when the BTF (**7**) pellet was placed above the salt (**1b**) pressed pellet (runs 7-8) as viewed in Table 2.

To obtain the heat of combustion contributed solely by the BTF (**7**) compound (ΔU_c^{exp}), the energy contributions from the combustion of the benzoic acid pellet (**8**) and the nitric acid formed were subtracted from the overall energy measured by the calorimeter from each combined BTF/BA combustion run as mentioned earlier (Section 2.2.5). This subtraction provided the observed experimentally determined BTF (**7**) heat of combustion (ΔU_c^{exp}) results displayed in Table 2. Averaging the BTF (**7**) observed experimental heat of combustion for runs 3-5 (Table 2), an experimental heat of combustion ($\Delta_c U^{\text{exp}}$) equal to $-(2827.17)$ cal/g with a relative standard deviation of 0.06% was obtained. Based on the molecular weight of BTF (**7**) (MW = 252.10 g/mol), an uncorrected molar enthalpy of combustion ($\Delta_c H^{\text{mol}}$) equal to $-(712.7)$ kcal/mol was obtained. Correcting for the six mole overall gas volume increase (Δn) during the combustion of BTF (**7**) seen in Equation (4),

converting this gas to standard conditions using Eq. (5), or as illustrated earlier in Eq. 1

with a calculated ΔnRT value of 3.6 kcal/mol, the observed heat of combustion ($\Delta_c U^{\text{exp}}$)

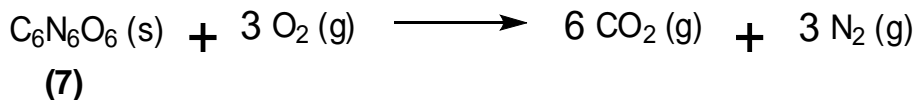
Table 2. Experimental enthalpy of combustion for stacked pelletized BTF (7)/BA (8) samples and re-crystallized $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (1b)/BTF (7) samples

Run No.	Sample Pellets (Top/Bottom)	Sample Masses (g)	Combined Combustion Energy (cal)	Nitric Acid (cal)	ΔU_c^{exp} of unknown (cal/g)	$\Delta_c U^{\text{exp}}$, Averaged (cal/g)
1	Benzoic Acid	1.4176	0	11.44	-6323.4955	-----
2	BA/BTF	1.016/0.8323	-6419.0880	26.73	-2783.9795	-----
3	BTF/BA	0.8104/1.0099	-6380.5482	27.15	-2827.9758	See Below
4	BTF/BA	0.8630/1.0056	-6353.3808	27.70	-2826.1345	See Below
5	BTF/BA	0.8452/0.9928	-6272.5104	29.65	-2826.3904	-2827.1669
6	BTF/Salt (1b)	1.4965/0.5089	-4230.8552	27.01	-9420.6004	-----
7	Salt (1b)/BTF	0.4632/1.6631	-4701.8613	28.54	-9633.8301	See Below
8	Salt (1b)/BA	0.4676/0.3383	-4701.8613	15.59	-9678.0925	-9655.9613

led to a BTF (7) standard molar enthalpy of combustion ($\Delta_c H^\circ$) equal to - (709.2)

kcal/mol or - (2967.3) kJ/mol. This experimentally determined standard enthalpy of

combustion ($\Delta_c H^\circ$) value exactly matched the BTF (7) condensed phase standard enthalpy of combustion



(4)

published in the NIST Standard Reference Database 69: *NIST Chemistry WebBook* of $-(2967 \pm 4)$ kJ/mol or $-(709.2 \pm 0.9)$ kcal/mol [16,17]. This exact BTF (**7**) standard enthalpy of combustion comparison further indicated that the calorimeter was properly standardized and suggested that the BTF compound (**7**) essentially was 100% pure. Note that the one pure benzoic acid (**8**) experimental run in Table 2 yielded an experimental heat of combustion ($\Delta_c U^{\text{exp}}$) equal to $-(6324)$ cal/g, which once again, is within the expected $-(6325 \text{ to } 6309)$ cal/g range derived by back calculation from the published NIST standard enthalpy of combustion value ($\Delta_c H^\circ$) of $-(3228 \pm 4)$ kJ.mol or $-(772 \pm 1)$ kcal/mol [16].

Next, we verified whether the BTF (**7**) combustion accelerant was needed to achieve the most efficient combustion for the $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (**1b**). Table 2 results for the combined 99.2 % pure $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]/\text{BTF}$ stacked pellets sample in runs 6 and 7 both provided higher observed experimental heat of combustion values ($\Delta_c U^{\text{exp}}$) than the $-(9094.42)$ cal/g value (Table 1) for the less pure 94.8% $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (**1a**) obtained in the absence of BTF (**7**) accelerant. However, the combined $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]/\text{BA}$ sample in run 8, where the benzoic acid (**8**) standard replaced the BTF (**7**) combustion accelerant, yielded an even higher observed experimental heat of combustion than any of the combined $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]/\text{BTF}$ sample runs 6-7 using the reported [12] BTF (**7**) combustion accelerant. This result offered a clue about the nature of the $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (**1b**) combustion behavior and efficiency.

The BTF (7) and benzoic acid (8) pellets appeared to have improved the overall [1AT3H]₂[*closo*-B₁₂H₁₂] salt (1b) combustion efficiency (runs 6-8); but, it also would be expected that the purer re-crystallized 99.2% [1AT3H]₂[*closo*-B₁₂H₁₂] salt (1b) should deliver a higher observed experimental heat of combustion value than the – (9094.42) cal/g value for the 94.8% pure [1AT3H]₂[*closo*-B₁₂H₁₂] salt (1a) in Table 1. To determine which of these factors, ancillary spike (accelerant) or salt (1) sample purity, might contribute more predominantly to a the higher observed experimental heat of combustion values observed for runs 6-8 of Table 2, three heat of combustion determinations were performed with only the 99.2% pure [1AT3H]₂[*closo*-B₁₂H₁₂] salt (1b) as seen in (Table 3).

Like the combustion bomb method employed with the original 94.8% pure [1AT3H]₂[*closo*-B₁₂H₁₂] salt (1a) in Table 1, quality control runs using only benzoic acid (8) were interspersed with runs made using only the re-crystallized 99.2% pure [1AT3H]₂[*closo*-B₁₂H₁₂] salt (1b) sample in Table 3. Again, the three experimental heat of combustion ($\Delta_c U^{\text{exp}}$) results for the benzoic acid (8) quality control runs produced an average value of –6316 cal/g corresponding to $\Delta_c H^\circ = - (3225) \text{ kJ/mol}$ or – (771.3) kcal/mol , which compared well with the published NIST standard value ($\Delta_c H^\circ = -(3228 \pm 4) \text{ kJ/mol}$ or – (772 \pm 1) kcal/mol for benzoic acid (8) [16].

Table 3. Observed experimental enthalpy of combustion for the re-crystallized 99.2% pure [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1b**)

Run No.	Chemical Sample	Sample Mass (g)	Nitric Acid (cal)	Experimental $\Delta_c U^{\text{exp}}$ (cal/g)	$\Delta_c U^{\text{exp}}$ 3 Run Averaged (cal/g)
Q. C. Standard	Benzoic Acid	1.0192	12.11	-6314.8902	-----
1	Salt (1b)	0.7178	10.72	-9693.7723	See Below
Q. C. Standard	Benzoic Acid	1.0154	11.42	-6314.7570	-----
Q. C. Standard	Benzoic Acid	1.0185	11.28	-6317.0204	-----
2	Salt (1b)	0.7103	12.70	-9692.2157	See Below
3	Salt (1b)	0.6616	11.14	-9685.1615	-9690.3832

The observed experimental heat of combustion results in Table 3, conducted only with [1ATH]₂[*closo*-B₁₂H₁₂] salt (**1b**), were reproducible and significantly higher than expected from the extrapolated 100% pure salt – (9593.27) cal/g value that the 94.8% salt (**1a**) sample would have been expected to reach. In runs 1-3, the experimental heat of combustion ($\Delta_c U^{\text{exp}}$) results also were higher than those obtained with either the BTF (7) “combustion accelerant,” or the benzoic acid (**8**) spike aid which ranged from – (9420.6 to 9678.1) cal/g for runs 6-8 in Table 2. The averaged $\Delta_c U^{\text{exp}}$ equaled – (9690.38) cal/g for the 99.2% pure [1-AT3H]₂[*closo*-B₁₂H₁₂] salt (**1b**) seen in Table 3. Unlike the [acyclinum]₂[*closo*-B₁₀H₁₀] salts (**4-6**), salt (**1b**) potentially underwent complete combustion without the need for a combustion accelerant, which when used, inexplicably inhibited achieving the best experimental heat of combustion for purer salt (**1b**). The higher $\Delta_c U^{\text{exp}}$ heat of combustion results, which revealed possible complete combustion

behavior for [1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1b**), resulted solely because of the increased purity attained by the aqueous re-crystallization of the original salt (**1a**). Based on the molecular weight for salt (**1b**), MW = 312.00 g/mol, an uncorrected standard molar enthalpy of combustion $\Delta_c H^\circ$ equal to – (3023.40) cal/mol was obtained. This calculated standard molar enthalpy of combustion for [1-AT3H]₂[*closo*-B₁₂H₁₂] salt (**1b**) was $\Delta_c H^\circ = - (3029.6 \pm 0.8)$ kcal/mol as illustrated in Eq. (5).

$$\begin{aligned} \text{From Table 3: } \Delta_c H^\circ_{\text{Salt 1b}} &= [-9690.38 \text{ cal/g}] \times [312.0 \text{ g/mol}] \times [1 \text{ kcal/1000 cal}] = -3023.40 \text{ kcal/mol;} \\ \text{From Eq. 1: } \Delta n &= \sum n_i (\text{gaseous products}) - \sum n_i (\text{gaseous reactants}) = -10.5 \text{ mol; then,} \\ \Delta nRT &= [-10.5 \text{ mol}] \times [1.986 \text{ cal/mol K}] \times [1 \text{ kcal/1000 cal}] \times [298.15 \text{ K}] = -6.22 \text{ kcal/mol; and,} \\ \Delta_c H^\circ_{\text{Salt 1b}} &= \Delta_c H^{\text{mol}}_{\text{salt 1b}} + \Delta nRT = [-3023.40 \text{ kcal/mol}] + [-6.22 \text{ kcal/mol}] = -3029.62 \text{ kcal/mol} \quad (5) \end{aligned}$$

Using the standard molar heat of formation values from the NIST Standard Reference Database 69 NIST Chemistry, *NIST Chemistry WebBook* [16] for the known reactants and products (*i.e.* $\Delta_f H^\circ \text{O}_2 \text{ gas} = 0$ kcal/mol; $\Delta_f H^\circ \text{H}_2\text{O liq} = - (68.315)$ kcal/mol; $\Delta_f H^\circ \text{CO}_2 \text{ gas} = - (94.054)$ kcal/mol; and, $\Delta_f H^\circ \text{H}_3\text{BO}_3 \text{ solid} = - (261.470)$ kcal/mol) seen in Eq. 2, the standard heat of formation for the 99.2% pure 1-amino-3H-1,2,3-triazolium icosahedral *closo*-dodecaborane salt (**1b**) or [1AT3H]₂[*closo*-B₁₂H₁₂] could be determined by Eq. 6 as equaling – (25.2) kJ/mol, – (6.03) kcal/mol, or – (0.019) kcal/g.

$$\begin{aligned} \text{From Eq. 2 and 5: } \Delta_f H^\circ_{\text{Salt 1b (s)}} &= 4 \times (-94.054 \text{ kcal/mol}) + 12 \times (-261.470 \text{ kcal/mol}) - (-3029.62 \text{ kcal/mol}) \\ &+ 7 \times (-68.315 \text{ kcal/mol}) = \mathbf{-6.03 \text{ kcal/mol}} \quad (-0.019 \text{ kcal/g}) \quad \mathbf{or} \quad -6.03 \text{ kcal/mol} \times 4.184 \text{ kJ/1 kcal} \\ &= \mathbf{-25.2 \text{ kJ/mol}} \quad (-0.086 \text{ kJ/g}) \quad (6) \end{aligned}$$

The experimental heat of combustion and resultant heat of formation results produced by the original 94.8% pure salt (**1a**) were very different from that obtained with the purer re-crystallized 99.2% salt (**1b**) viewed in Table 4. In fact, it is worth noting that the linear extrapolated 94.8% pure salt (**1a**) heat of formation ($\Delta_f H^\circ$) to a 100% purity was still slightly over six times lower than that experimentally determined for the 99.2% pure salt (**1b**) which **was** re-crystallized from salt (**1a**). This demonstrated a critical need to obtain, as closely as possible, a 100% sample purity when attempting to determine these key thermochemical values.

Table 4. Experimental heat of combustion, standard molar enthalpy of combustion, and standard heat of formation as a function of $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (**1**) purity.

Salt (1) purity (%)	$\Delta_c U^{\text{exp}}$ ht. of comb. (cal/g)	$\Delta_c H^\circ$ enthp. of comb. (kcal/mol)	$\Delta_f H^\circ$ std. ht. of form. (kcal/mol)	$\Delta_f H^\circ$ std. ht. of form. (kJ/mol)
94.8% salt (1a)	−9094.4	−2843.6	−204.4	−855.2
100% salt (1a) <u>extrapolated</u> value	−9593.3	−2999.3	−36.3	−152.0
99.2% salt (1b)	−9690.4	−3039.6	−6.0	−25.2

The 4.4% purity increase with the re-crystallized 99.2 % $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (**1b**) increased the heat of formation 830 kJ/mol (198.4 kcal/mol) more positive than the original 94.8% pure $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (**1a**). While it would be interesting to determine the heat of formation for a 100% pure $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (**1**) sample,

or to extrapolate it from salt (**1b**) data, the magnitude for any heat of formation increase would depend on whether a graphic plot of sample purity versus either the experimental heat of combustion, or the standard molar heat of formation, followed a predictable linear, asymptotic, or other functional curve fitting model. With the limited amount of 1[AT3H]₂[*closo*-B₁₂H₁₂] salt (**1**) sample, task time constraints, and funding/manpower resources, a more complex investigation to study such a graphic plot could not be pursued.

The 1AT3H]₂[*closo*-B₁₂H₁₂] salt (**1**) illustrated the noticeable energy increase that members of the uniquely new binary heterocyclium *closo*-dodecaborane salt family [1-3] provided when compared to acyclium *closo*-decaborane salts (**4-6**) illustrated in Table 5. It is postulated that this higher energy content for salt (**1**), to a noticeable extent, resulted from the presence of the protonated heterocyclium 1-amino-3-H-1,2,3-triazolium cation, [1AT3H]⁺. Possible future syntheses of binary [heterocyclium]₂[*closo*-B₁₀H₁₀] salts, that contain analogous heterocyclium cations already paired with the [*closo*-B₁₂H₁₂]²⁻ di-anion [1-3], would directly quantify heat of formation differences between the analogous heterocyclium [B₁₂H₁₂] and potentially synthesized heterocyclium [B₁₀H₁₀] *closo*-borane salts.

Table 5. Standard heat of formation comparison of heterocyclium and acyclinum *closo*-borane-based salts

Borane-Based Salt (Number)	Di-[1AT3H] ₂ [<i>closo</i> -B ₁₂ H ₁₂] (1b)	Di-ammonium [<i>closo</i> -B ₁₀ H ₁₀] (4)	Di-hydrazinium [<i>closo</i> -B ₁₀ H ₁₀] (5)	Di-guanidinium [<i>closo</i> -B ₁₀ H ₁₀] (6)
$\Delta_f H^\circ$ (kcal/mol)	- 6.0 ± 0.8 [This work]	-87.7 ± 0.8 [13] -85.8 ± 2.5 [14]	-32.9 ± 1.6 [13]	-97.9 ± 1.8 [13]
$\Delta_f H^\circ$ (kJ/mol)	-25.1	-366.9 -359.0	-137.6	-409.6

4. Conclusions

A series of high energy binary heterocyclium icosahedral *closo*-dodecaborane salts both with limited water solubility and highly water soluble behavior recently have been reported [1-3]. The standard heat of combustion was determined for one of these unique new salts **1** of limited water solubility where two 1-amino-3H-1,2,3-triazolium cations, $[1AT3H]^+$, are paired with the icosahedral-shaped $[closo-B_{12}H_{12}]^{2-}$ dodecaborane di-anion. Combustion calorimetry with this $[1AT3H]_2[closo-B_{12}H_{12}]$ salt (**1**), using a reliable isoperibolic combustion method unveiled the first established standard molar enthalpy of combustion and heat of formation results to be obtained with either a heterocyclium *closo*-borane-based salt or with a salt containing the *closo*-dodecaborane $[closo-B_{12}H_{12}]^{2-}$ di-anion. Data obtained from this $[1AT3H]_2[closo-B_{12}H_{12}]$ salt (**1**) at two different purities emphasized the highly dependent relationship between the heat of formation and verified salt product purity. The purer 99.2% $[1AT3H]_2[closo-B_{12}H_{12}]$ salt (**1**) revealed a standard molar enthalpy of combustion equal to $-(3029.6 \pm 0.8)$ kcal/mol with an associated standard heat of formation $-(25.1 \pm 3.5)$ kJ/mol or $-(6.03 \pm 0.8)$ kcal/mol which would be higher for a 100% pure salt (**1**) sample. Previously, only two enthalpy of combustion and resultant heat of formation values were reported for borane-based salts that contained two acyclinum ammonium (**4**) [12,13], hydrazinium (**5**) [12], or guanidinium (**6**) [12] cations which were stoichiometrically paired with the smaller $[closo-B_{10}H_{10}]^{2-}$ decaborane di-anion homologue. While these acyclinum *closo*-

decaborane salts (**4-6**) required the benzotrifuroxan (BTF) compound (**7**) as a combustion accelerant to achieve complete combustion, the $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (**1**) needed no such accelerant. The most efficient combustion behavior for salt (**1**) proceeded in the absence of any combustion accelerant. A comparison of the subject binary 99.2 % pure salt (**1**) with the three binary acyclinium *closo*-decaborane, $[\text{acyclinium}]_2[\text{closo-B}_{10}\text{H}_{10}]$ salts (**4-6**), demonstrated that binary heterocyclium *closo*-dodecaborane salt (**1**) possessed a significantly higher standard enthalpy of combustion and heat of formation. This recently synthesized $[1\text{AT3H}]_2[\text{closo-B}_{12}\text{H}_{12}]$ salt (**1**) [1] revealed a high energy material that displays notable combustion and initiation properties [2,3,8].

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